

TABLE 1. Equilibrium Acidity Scale Valid in 1,2-Dichloroethane As Solvent (Acidity Increases Downwards)<sup>a</sup>

No	Acid	pK <sub>a</sub> (DCE)	Directly measured ΔpK <sub>b</sub> values in DCE <sup>a</sup>	pK <sub>a</sub> (MeCN) <sup>b</sup>
1	Picric acid <sup>c</sup>	0.0		11.0
2	HCl	-0.4	-0.73 → -0.71	10.6
3	2,3,4,6-(CF <sub>3</sub> ) <sub>5</sub> -C <sub>6</sub> H-CH(CN) <sub>2</sub>	-0.7	1.48 → 0.36 → 1.09	10.3
4	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> NHTos <sup>d</sup>	-1.5	0.77 → 0.74 → 2.08 → 1.00	9.6
5	HNO <sub>3</sub>	-1.7	0.28 → 1.78	9.4
6	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> NHSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -4-Cl	-2.4	-1.13 → 1.01 → 0.88 → 0.24 → 1.08	8.8
7	H <sub>2</sub> SO <sub>4</sub>	-2.5	0.12 → 1.26	8.7
8	C <sub>6</sub> (CF <sub>3</sub> ) <sub>2</sub> CH(CN) <sub>2</sub>	-2.6	1.02 → 1.02 → 1.05	8.6
9	(4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -SO <sub>2</sub> ) <sub>2</sub> NH	-3.7	1.48 → 0.47 → 0.80	7.7
10	3-NO <sub>2</sub> -4-Cl-C <sub>6</sub> H <sub>3</sub> SO <sub>2</sub> NHSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -4-NO <sub>2</sub>	-4.1	0.36 → 1.35 → 0.93 → 0.62	7.3
11	(3-NO <sub>2</sub> -4-Cl-C <sub>6</sub> H <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> NH	-4.5	0.39 → 0.19 → 1.03 → 0.80	7.0
12	HBr	-4.9	0.19 → 1.03	6.6
13	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH(CN) <sub>2</sub>	-5.1	0.80 → 1.33	6.4
14	2,4,6-(SO <sub>2</sub> F) <sub>3</sub> -Phenol	-5.9	0.64 → 1.33	5.7
15	2,4,6-Tf <sub>3</sub> -Phenol <sup>e</sup>	-6.4	0.94 → 0.42 → 1.14 → 1.12	5.2
16	CH(CN) <sub>3</sub>	-6.5	0.33 → 0.65 → 0.51 → 0.05	5.1
17	4-Cl-C <sub>6</sub> H <sub>4</sub> SO(=NTf) <sub>2</sub> NHTos	-6.8	0.20 → 0.24 → 0.51 → 0.05	4.9
18	NH <sub>2</sub> -TCNP <sup>f</sup>	-6.8	0.20 → 0.24 → 0.51 → 0.05	4.9
19	2,3,5-tricyanocyclopentadiene	-7.0	0.67 → 0.84	4.7
20	Pentacyanophenol	-7.6	1.77 → 1.56 → 1.54 → 0.98 → 1.13 → 1.00	4.2
21	4-Cl-C <sub>6</sub> H <sub>4</sub> SO(=NTf) <sub>2</sub> NHSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -4-Cl	-7.7	1.10 → 0.93 → 1.04 → 1.01 → 0.96 → 0.81 → 0.90	4.1
22	HI	-7.7	0.13 → 0.09 → 0.13 → 0.02	4.1
23	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> NHTf	-7.8	0.13 → 0.09 → 0.13 → 0.02	4.0
24	Me-TCNP	-8.6	0.13 → 0.09 → 0.13 → 0.02	3.3
25	3,4-(MeO) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> -TCNP	-8.7	0.13 → 0.09 → 0.13 → 0.02	3.2
26	4-MeO-C <sub>6</sub> H <sub>4</sub> -TCNP	-8.7	0.13 → 0.09 → 0.13 → 0.02	3.2
27	C(CN) <sub>2</sub> =C(CN)OH	-8.8	0.28 → 0.46 → 1.61 → 0.24	3.1
28	4-Cl-C <sub>6</sub> H <sub>4</sub> SO(=NTf) <sub>2</sub> NHSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub>	-8.9	0.22 → 0.67 → 0.59 → 0.74 → 0.06	3.0
29	2,4-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> SO <sub>2</sub> OH	-8.9	0.67 → 0.59 → 0.60 → 0.74 → 0.06	3.0
30	C <sub>6</sub> F <sub>5</sub> CH(Tf) <sub>2</sub>	-9.0	0.59 → 0.60 → 0.74 → 0.06	2.9
31	HB(CN)(CF <sub>3</sub> ) <sub>3</sub>	-9.3	0.47 → 1.33 → 0.13 → 0.44 → 0.52	2.6
32	Ph-TCNP	-9.4	0.83 → 1.56 → 1.57 → 1.62 → 1.23	2.5
33	HBf <sub>4</sub>	-10.3	1.06 → 0.26 → 1.34	1.8
34	FSO <sub>2</sub> OH	-10.5	0.01 → 0.21 → 0.22	1.5
35	3-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -TCNP	-10.5	0.58 → 0.60 → 0.22	1.5
36	H-TCNP	-10.7	0.73 → 0.78 → 0.46	1.3
37	[C <sub>6</sub> H <sub>5</sub> SO(=NTf)] <sub>2</sub> NH	-11.1	0.73 → 0.78 → 0.46	1.0
38	[(C <sub>2</sub> F <sub>5</sub> ) <sub>2</sub> PO] <sub>2</sub> NH	-11.3	0.89 → 0.29 → 0.28 → 0.91 → 0.93	0.8
39	2,4,6-(NO <sub>2</sub> ) <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> SO <sub>2</sub> OH	-11.3	0.44 → 0.10 → 0.12 → 0.07 → 0.09 → 0.47 → 0.49	0.8
40	[C(CN) <sub>2</sub> =C(CN)] <sub>2</sub> CH <sub>2</sub>	-11.4	0.04 → 0.32 → 0.47 → 0.09 → 0.49	0.7
41	TfOH	-11.4	0.04 → 0.32 → 0.47 → 0.09 → 0.49	0.7
42	C <sub>6</sub> H <sub>5</sub> SO(=NTf) <sub>2</sub> NHTf	-11.5	0.40 → 0.32 → 0.47 → 0.09 → 0.49	0.7
43	TfCH(CN) <sub>2</sub>	-11.6	0.36 → 0.20 → 0.25	0.6
44	Br-TCNP	-11.8	0.06 → 0.10 → 0.67 → 0.63 → 0.73 → 0.75	0.4
45	[C(CN) <sub>2</sub> =C(CN)] <sub>2</sub> NH	-11.8	0.06 → 0.10 → 0.67 → 0.63 → 0.73 → 0.75	0.3
46	3,5-(CF <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> -TCNP	-11.8	0.21 → 0.45 → 0.19	0.4
47	Tf <sub>2</sub> NH	-11.9	0.30 → 0.31	0.3
48	4-Cl-C <sub>6</sub> H <sub>4</sub> SO(=NTf) <sub>2</sub> NHTf	-12.1	0.01 → 0.15 → 0.36 → 0.46 → 0.42	0.1
49	Cl-TCNP	-12.1	0.01 → 0.15 → 0.36 → 0.46 → 0.42	0.1
50	(C <sub>3</sub> F <sub>7</sub> SO <sub>2</sub> ) <sub>2</sub> NH	-12.2	0.10 → 0.13 → 0.21 → 0.40 → 0.29	0.1
51	(C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> ) <sub>2</sub> NH	-12.2	0.69 → 0.19 → 0.10 → 0.27 → 1.29	0.0
52	CN-CH <sub>2</sub> -TCNP	-12.3	1.06 → 0.92 → 0.02 → 0.47 → 0.44 → 1.04 → 0.93	-0.1
53	(C <sub>2</sub> F <sub>5</sub> SO <sub>2</sub> ) <sub>2</sub> NH	-12.3	1.06 → 1.05 → 1.06 → 0.72 → 0.47 → 0.44 → 1.04 → 0.93	-0.1
54	CF <sub>3</sub> -TCNP	-12.7	0.80 → 0.77 → 0.96	-0.5
55	HClO <sub>4</sub>	-13.0	0.80 → 0.40 → 1.04	-0.7
56	CF <sub>3</sub> (CF <sub>2</sub> SO <sub>2</sub> ) <sub>2</sub> NH	-13.1	0.89 → 0.11 → 0.86 → 0.56 → 0.07	-0.8
57	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> SO(=NTf) <sub>2</sub> NHTf	-13.1	0.89 → 0.11 → 0.86 → 0.56 → 0.07	-0.8
58	HB(CN) <sub>4</sub>	-13.3	0.44 → 1.78	-1.0
59	(FSO <sub>2</sub> ) <sub>2</sub> CH	-13.6	1.78 → 2.16	-1.2
60	Tf <sub>2</sub> CH(CN)	-14.9	1.46 → 1.73 → 0.22	-2.4
61	2,3,4,5-tetracyanocyclopentadiene	-15.1	0.40 → 0.21 → 0.23	-2.6
62	CN-TCNP	-15.3	0.21 → 0.23	-2.8
63	Tf <sub>3</sub> CH <sup>g</sup>	-16.4		-3.7
64	CF <sub>3</sub> SO(=NTf) <sub>2</sub> NHTf <sup>g</sup>	-18		-5

<sup>a</sup>Directly measured relative acidity values in DCE. <sup>b</sup>Predicted pK<sub>a</sub> values of MeCN (see the SI for details). <sup>c</sup>pK<sub>a</sub> value of picric acid is arbitrarily set to 0. <sup>d</sup>Tos represents the 4-Me-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>- group. <sup>e</sup>Tf represents the CF<sub>3</sub>SO<sub>2</sub>- group. <sup>f</sup>X-TCNP represents 2-X-1,1,3,3-tetracyanopropene. <sup>g</sup>Estimated DCE pK<sub>a</sub> values, see text. <sup>h</sup>Scheme 1 shows compound and group structures.